

Spectrophotometric Determination of the Ionization Constant of Dimethylpicric Acid (2,4,6-Trinitro-3,5-xyleneol) in Water at 25 °C

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The ionization constant of dimethylpicric acid (2,4,6-trinitro-3,5-xyleneol) in water at 25 °C has been determined by a spectrophotometric method. The pK value 1.38 ($K \approx 0.042$) was obtained. Potentiometric titrations, although less precise, yielded a pK value of the same magnitude.

1. Introduction

Moore and Peck [1]² determined the pK of dimethylpicric acid by potentiometric titration, and reported the value 3.3. On the assumption that the effects of substituents on the ionization constant of phenol are additive, data on the ionization constants of phenol and its monosubstituted derivatives [2, 3] can be used to calculate 1.76 as an approximate pK value for dimethylpicric acid. Alternatively, data for 2,6-dinitrophenol [4], p -nitrophenol, and 3,5-xyleneol [5] can be combined to give another estimate, 1.05. Combining data for 2,6-dinitrophenol and 4-nitro-3,5-xyleneol [6] yields the estimate 1.96, whereas utilizing data for 2,4-dinitrophenol [7], o -nitrophenol, and 3,5-xyleneol leads to the value 1.50. These four estimates, even though not in close agreement, suggest that dimethylpicric acid may be too strong for a reliable application of the method previously used for estimating pK [1]. Redetermination of its pK by a different method is therefore desirable.

This paper describes the determination of pK for dimethylpicric acid by a spectrophotometric procedure.

2. Experimental Procedure

2.1. Dimethylpicric Acid

Dimethylpicric acid (2,4,6-trinitro-3,5-xyleneol) was prepared by nitrating 3,5-xyleneol [1]. After isolation by conventional procedures, the product was finally recrystallized from cyclohexane and dried at 90 °C; mp 106.4 to 106.8 °C.³ Potentiometric weight-titrations indicated a purity of not less than 99.9 percent.

2.2. Determination of pK Value by Spectrophotometry

The pK value was calculated from the equation

$$pK = -\log[H^+] - 2 \log \gamma_{\pm} - \log[(D - D_1)/(D_2 - D)], \quad (1)$$

in which $[H^+]$ signifies the total hydrogen ion concentration in moles per liter, γ_{\pm} is taken as the mean activity coefficient of aqueous hydrochloric acid of equivalent molarity,⁴ and the symbols D_1 , D_2 , and D denote the spectral absorbances (optical densities) of solutions containing the same total molar concentration of dimethylpicric acid present as nonionized molecules, ionized molecules, or mixtures of the two, respectively. Dimethylpicric acid is so nearly completely ionized in water at the concentration used ($5.004 \times 10^{-5} M$) in determining D_2 and D_1 values that addition of sodium hydroxide ($pH \approx 12$) did not measurably alter the absorption curve. In determining D_1 values, the dimethylpicric acid was dissolved in $\sim 2.2-M$ hydrochloric acid. The measurements of D values were made with solutions containing $1.250 \times 10^{-4} M$ dimethylpicric acid together with hydrochloric acid in concentrations varying from $\sim 0.01-M$ to $\sim 0.1-M$. The absorbances were obtained with a Beckman Model DU quartz spectrophotometer.

3. Results and Discussion

3.1. Spectrophotometric Determination of pK

Absorption curves for dimethylpicric acid in alkaline and acidic solutions are presented in figure 1. In measuring the absorption of dimethylpicric acid in hydrochloric acid solutions which varied from $1-M$ to $6-M$ in concentration, it was observed that with increasing concentrations of hydrochloric acid the absorption in the region from about 380 $m\mu$ to about 420 $m\mu$ gradually decreased to constant values. At

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² Figures in brackets indicate the literature references at the end of this paper.

³ The mp reported in [1] was 106.5 °C (uncor.).

⁴ Values of γ_{\pm} were interpolated from a graph of the mean activity coefficient of hydrochloric acid at 25 ° versus its molality (see [8], table 11-4-1A, p. 547). Harned and Ehler's function derived for 1:1 electrolytes in water was used to convert molarities of acid to the corresponding molalities (see table 12-1-1A of [8]).

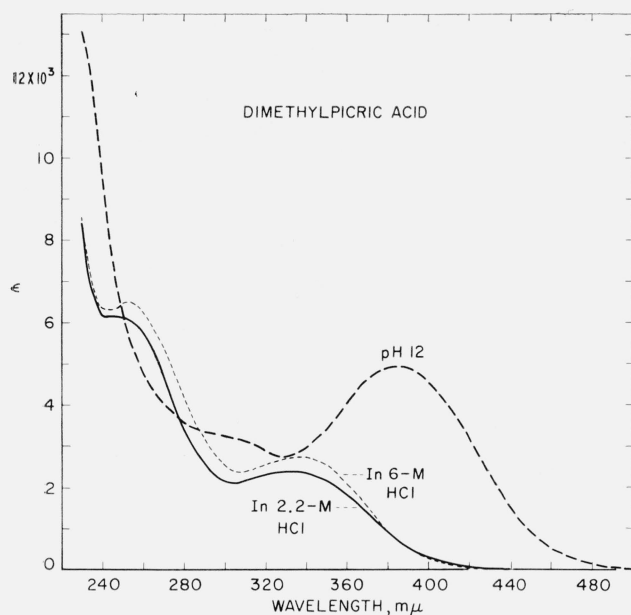


FIGURE 1. Spectral absorption curves of dimethylpicric acid (2,4,6-trinitro-3,5-xenol) in aqueous acid (approx. 2.2-M HCl and approx. 6-M HCl) and in aqueous alkali (NaOH, pH \approx 12).

The curve for the solution containing 2.2-M HCl is believed to approximate closely the spectral absorption of nonionized dimethylpicric acid.

wavelengths shorter than 380 mμ, however, the absorption at first decreased and then progressively increased. It seems unlikely that this secondary change can be attributed to an impurity in the solutions; possibly, it involves nitro groups. The curves obtained for solutions of dimethylpicric acid in 2.2-M and 6-M hydrochloric acid illustrate the secondary change. The curve for 2.2-M hydrochloric acid solution is believed to approximate closely the spectral absorption of nonionized dimethylpicric acid.

In determining pK , absorbance values at 390, 400, and 410 mμ were used. Since the values of D_1 at these wavelengths are low and do not vary measurably with concentrations of hydrochloric acid greater than 3-M, the secondary change in absorption is believed not to have caused errors in determining pK .

The tabulated data and results are presented in table 1. The average pK value obtained was 1.376, or approximately 1.38 (corresponding to an ionization constant of about 0.042). This pK value falls within the range of the various estimated constants (see sec. 1).

3.2. Attempted Potentiometric Determination of pK

Attempts were made to determine pK by titrating 0.005-M dimethylpicric acid with alkali about 10 times as concentrated, using glass and saturated calomel electrodes [9].⁵ This concentration of dimethylpicric acid is close to the limit of its solubility in water at 25 °C. Values of pK were calculated

⁵ In part of the titrations a Precision-Shell titrometer was used; in others, a Beckman pH meter, model G.

from the equation

$$pK = pH - \log \left\{ \frac{([B^-] + [H^+])}{([HB] - [H^+])} \right\} + 0.5115 \sqrt{I} / (1 + 1.5 \sqrt{I}). \quad (2)$$

The pK values obtained from eight titrations varied from 1.26 to 1.66, yielding the average value 1.49. Considering the limited solubility and relatively high acidity of dimethylpicric acid, high precision and accuracy by potentiometric titration do not appear feasible for this compound. However, the average pK value obtained in this work agrees in general magnitude with the value determined spectrophotometrically.

TABLE 1. Ionization constant of dimethylpicric acid (2,4,6-trinitro-3,5-xenol) in water at 25 °C^{a,b}

Concentration of HCl ^b	D	$\log[(D-D_1)/(D_2-D)]$	$-\log[H^+]$ ^b	$-2 \log \gamma_{\pm}$	pK
$\lambda = 390 \text{ m}\mu \quad D_1 = 0.064, D_2 = 0.612$					
0.0102	0.521	0.701	1.989	0.087	1.375
.0203	.462	.424	1.691	.115	1.382
.0332	.413	.244	1.478	.140	1.374
.0519	.359	.067	1.284	.164	1.381
.0623	.340	.006	1.205	.174	1.373
.104	.277	-.197	0.984	.200	1.381
$\lambda = 400 \text{ m}\mu \quad D_1 = 0.029, D_2 = 0.568$					
0.0102	0.477	0.692	1.989	0.087	1.384
.0203	.422	.430	1.691	.115	1.376
.0332	.373	.246	1.478	.140	1.372
.0519	.321	.073	1.284	.164	1.375
.0623	.302	.011	1.205	.174	1.368
.104	.244	-.178	0.984	.200	1.362
$\lambda = 410 \text{ m}\mu \quad D_1 = 0.011, D_2 = 0.495$					
0.0102	0.411	0.678	1.989	0.087	1.398
.0203	.366	.440	1.691	.115	1.366
.0332	.318	.239	1.478	.140	1.379
.0519	.271	.065	1.284	.164	1.383
.0623	.254	.003	1.205	.174	1.376
.104	.203	-.182	0.984	.200	1.366
Average					1.376
					$K = 0.042$

^a Concentration of dimethylpicric acid, 1.250×10^{-4} M. Optical absorption cells were 1 cm in length.

^b All concentrations are in moles per liter.

4. References

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